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Methane release through resuspension of littoral sediment

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Abstract. Sediment in the littoral zone of lakes is frequently disturbed by wave action or bioturbation, resulting in sediment resuspension. In undisturbed sediment, methanotrophic bacteria efficiently reduce the diffusive flux of methane into the water column. In a microcosm study, the resuspension of littoral sediment was simulated in sediment cores for a winter (n = 3) and a summer situation (n = 3). The erosion of surface sediment resulted in a large flux of methane into the overlying water (207 ± 176 μmol h^{-1} m^{-2} in winter and 73 ± 18 μmol h^{-1} m^{-2} in summer). Only a minor part (16 ± 7%) of the methane released was oxidized by methanotrophic bacteria, whereas the major part escaped into the water column. Only 6–16% of the littoral zone has to be resuspended to reach the same flux as from undisturbed littoral sediment. For the daily flux, a sediment resuspension has to last 1–4 h to reach the undisturbed daily flux. The study reveals the important role of sediment resuspension in the littoral methane cycle as an intense but variable source of methane of largely unknown magnitude.

Introduction

Methane is an important greenhouse gas. Its concentration in the atmosphere has increased through the last few decades and appears to have levelled off since 2000 at a global average of 1750 ppb (http://www.cmdl.noaa.gov/ccgg/index.html). The contribution of freshwaters to the total natural methane emission is around 3% (Lelieveld et al. 1998). However, although the major source terms of atmospheric methane have probably been identified, especially the biospheric sources are highly variable in space and time and the strengths of these sources are therefore difficult to assess (IPCC 2001).

In freshwater sediments, anaerobic degradation of organic matter leads, to a large extent, to methane production. Therefore methane accumulates, often to supersaturation, especially in littoral sediments with high organic input and temporally high temperatures (Thebrath et al. 1993). Aerobic methane oxidation at the sediment surface acts as an efficient biofilter, and only a few percent of the originally produced methane is released into the water column (Frenzel et al. 1990).

Aerobic methane-oxidizing bacteria live at the sediment surface in counter gradients of methane diffusing upwards from deeper sediment layers and oxygen diffusing into the sediment from the water column. However, surface sediments are often resuspended and mixed into the water by currents and wind-induced waves or by the action of ships' propellers (Schoellhamer 1996). In addition, benthivorous fish may cause local resuspension events (Shormann and Cotner 1997). In contrast, freshwater macrophytes disperse wave energy and reduce sediment resuspension (Wetzel 2001).

With resuspension, the top layer of the sediment down to a few mm to cm is mixed into the water column, leading to a pulsed transport of reduced compounds, nutrients (Spagnoli and Bergamini 1997) and, most probably also of methane, into the water column. However, the methane oxidizing bacteria are also resuspended and therefore displaced from their sediment layer to an oxygen-saturated environment with low methane supply.

In this microcosm study, the effects of sediment resuspension on the methane flux in the littoral zone of Lake Constance, Germany, were investigated. Macrophytes have a profound impact on the methane cycle, but also reduce sediment resuspension, therefore an exposed study site with sparse vegetation was chosen. The study focused on the questions (i) how much methane is released during a suspension event and (ii) to what extent resuspended methane-oxidizing bacteria in the water column are able to buffer this pulsed methane release.

Materials and methods

Study site and sediment sampling

Experiments were carried out with sediment from the lower infralittoral zone ('Litoralgarten', 47°41′N, 9°12′E) of the Überlinger See, a fjord-like bay of Lake Constance, Germany. Macrophyte growth is sparse at this exposed site, and care was taken to sample only cores with no macrophytes. The sediment consisted of fine sand with a porosity of 0.62. Sediment cores (Ø 8 cm, length 37 cm) were taken with a modified sediment corer (Tessenow et al. 1975) in January/February and again in September 2002 at 2–4 m water depth. The water overlying the sediment cores was siphoned off until a 0.5 cm layer of water remained. Cores were kept at 7.2 ± 0.6 °C (winter) or 14 ± 0.2 °C (summer) in the dark.

Methane concentrations in sediments and water column

Parallel to the laboratory experiments, methane concentrations were also measured *in situ* in the water column and in the sediment at the study site. To sample the water column, samples (n = 11 and 13 in winter and summer, respectively) were taken by scuba with 100 ml syringes at 10–50 cm above the sediment and were processed as described below. Sediment cores were taken as described above. Immediately after retrieval, each sediment core (n = 2 in winter and $n = 3$ in summer) was subsampled at 1 cm intervals from the surface to 5 cm depth, followed by 2.5 cm intervals down to its maximal depth. With a cut-off syringe, 2 ml of sediment was transferred into a 60 ml glass vial filled with 10 ml of saturated NaCl solution. The top 5 cm of sediment were sampled in triplicate with three syringes. The headspace was then analyzed for methane (Kiene and Capone 1985). All samples were stored upside down and analyzed within 6 weeks.

In spring 2004 an underwater methane sensor (Capsum, Geesthacht, Germany and a loan of J. Greinert, Geomar, Kiel) was deployed with an under water station (with photo camera, temperature and light loggers, www.unikonstanz/fenster-zum-see) at the study site to record *in situ* methane concentrations in a high temporal dilution (1 min). At the sensor, methane diffuses from the water through a special membrane to the detector. The adsorption of methane to the membrane leads to modification of the resistance, which is recorded by the detector. Data were smoothed with a running average over 10 min. The sensor data were calibrated against triplicate water samples analyzed with headspace analysis and gas chromatograph ($n = 8$).

Experiments with continuous water flow microcosms

One experiment consisted of one control core (no resuspension) and one treatment core with sediment resuspension. Three experiments were performed in winter and again three experiments in summer. Experiments were performed at 7.2 ± 0.6 °C (winter) or 14 ± 0.2 °C (summer) in the dark. These temperatures are close to the *in situ* temperatures at the study site (Ph. Fischer, unpublished data).

All sediment cores (control and treatment) were irrigated continuously with filtered lake water (0.45 μm) by peristaltic pumps. The water was stored in 25 l polyethylene reservoirs and was aerated heavily to ensure 100% oxygen saturation. The water inlet to the cores was a curved glass tube placed horizontally, 0.5 cm above the sediment surface, thus inducing a weak circular current (0.381–0.400 $\mathrm{l\ h^{-1}}$) and continuous mixing of the water column (0.5 l). The water outlet was at the top of the core. All tubes and connections were of isoversinic and glass to minimize gas diffusion, in or out of the system. In the resuspension cores, a model ship's propeller was fixed in the centre of the core at the level of the water inlet tube.

The experiment was initiated by a 12-h pre-incubation phase for all cores. Then the stirring was started in the treatment core with a constant speed for 30 s. This eroded the sediment down to the depth of 5 mm. The mixing speed was then reduced to keep the sediment in suspension. These settings were chosen after preliminary experiments to test which propeller speeds were needed for sediment erosion and suspension. The propeller was stopped after 1.5 h. The experiment was stopped when the oxygen concentration in the post-suspension phase reached the level of the pre-incubation phase (6–8 h).

Water samples from the outlets of the control and treatment cores, as well as from the reservoir (inflowing water), were taken every 60 min during the pre-incubation phase (no resuspension), every 11 min during the suspension phase and every 50 min during the post-suspension phase. Water samples were analyzed for concentrations of methane, oxygen, and suspended solids. Additionally, at the end of the experiments, the methane concentration of the sediment was determined in two control cores.

Analytical methods

For methane measurement 15 ml water samples were taken from the core outlet with a glass syringe and transferred into serum bottles closed with butyl rubber stoppers. The addition of 4 g NaCl stopped biological activity and degassed the water samples. Methane was analyzed with a Carlo Erba gas chromatograph (GC 6000) equipped with a flame ionization detector and a molecular sieve column (5 Å, 60/80 mesh, Serva). The temperatures of the oven, the injector and detector were 120, 150, and 150 °C, respectively. The carrier gas (N_2) flow was 38 ml min^{-1}, 27 ml min^{-1} H_2 and 270 ml min^{-1} synthetic air.

The oxygen concentration [mg l^{-1}] in the outlet water was measured online with a polarographic oxygen probe (WTW OXY-340i) to an accuracy of 0.1 mg l^{-1}.

The water samples taken for determination of suspended solids (80–100 ml) were stored frozen. For determination of their suspended solid content they were filtered through pre-dried glass fibre filters (GF 6, Schleicher & Schuell) dried at 105 °C for 2 h, and then weighed.

Calculations

Methane flux in the cores

The measured methane flux from the sediment core into the water column was calculated using the formula:

$$J_M = (c_{in} - c_{out}) \cdot f \cdot A^{-1} \; [\mu\text{mol}\,\text{h}^{-1}\,\text{m}^{-2}]$$

Methane concentrations were measured in the inflowing (c_{in}) and in the outflowing (c_{out}) water. The difference between the two concentrations [μmol l^{-1}] multiplied by the flow rate of the water (f, l h^{-1}) gave the methane release (or consumption) rate. The methane flux rates (J_M) from the sediments were expressed per square meter (core diameter A in the equation above).

The diffusive methane flux (J_D) was calculated from methane concentrations in pore water using Fick's first law: $J_D = -D_s \cdot Ø \cdot (dc/dz)$ [μmol h^{-1} m^{-2}], with Ø = porosity of the sediment (0.62), D_s = sediment diffusion coefficient, and dc/dz = the measured methane concentration gradient in the top centimeters. The bulk sediment diffusion coefficient (D_s) was calculated from the molecular diffusion coefficient (D) by correction for porosity and tortuosity using the empirical equation ($D_s = D \cdot Ø^2$) with $D_{14°} = 1.51 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$ (Broecker and Peng 1974).

Dilution of methane in the continuous water flow microcosm

In the inflow water methane concentration was lower than in the core water, which diluted the methane concentration in the water column of the cores. The dilution of methane (f_{dil}) in the water column over time was calculated to be

$$c_t = c_R - (c_R - c_0) \cdot \exp(-f \cdot t \cdot V^{-1})$$

With c_t = the methane concentration at a certain time, c_R = the methane concentration of the inflowing water from the reservoir (0.16 and 0.19 μmol $\mathrm{l^{-1}}$ for the winter and summer experiments), c_0 = the initial concentration of methane in the water column of the cores, f = the flow rate of the water (0.381–0.400 l $\mathrm{h^{-1}}$), t = time and V = the water volume of the cores (0.503 l).

Estimation of the methane oxidation rate in the continuous water flow microcosm

The decrease of methane with time in the continuous water flow microcosm can be described by four functions: (1) the measured methane concentration in the outflowing water (f_{meas}), (2) the dilution and leaks in the experimental set-up ($f_{\mathrm{dil\ +\ loss}}$), (3) the potential methane oxidation rate (f_{slurry}) (calculated from the slurry experiment) and only for the calculations, (4) hypothetically no decrease of methane (f_{hypo}). Based on the dilution rate 3 h after the propeller was stopped, the methane concentrations should reach the initial values of the pre-incubation phase. Therefore the area under the curves was integrated for the time span of 3 h ($\int_{0\,h}^{3\,h}$ meas, $\int_{0\,h}^{3\,h}$ dil + loss, $\int_{0\,h}^{3\,h}$ slurry and $\int_{0\,h}^{3\,h}$ hypo). The difference between the measured and the expected methane decrease can be attributed to microbial methane oxidation (MOX$_{\mathrm{exp}}$ [μmol $\mathrm{l^{-1}}$] = $\int_{0}^{3\,h}$ dil+ loss − $\int_{0\,h}^{3\,h}$ meas). Additionally, the potential microbial methane oxidation rate (as calculated from the slurry experiment) was applied to the microcosm (MOX$_{\mathrm{pot}}$ [μmol $\mathrm{l^{-1}}$] = $\int_{0}^{3\,h}$ hypo − $\int_{0\,h}^{3\,h}$ slurry). Both methane oxidation rates were related to the real loss ($\int_{0\,h}^{3\,h}$ hypo − $\int_{0\,h}^{3\,h}$ meas = 100%). For this model it is assumed that no methane is produced and that – comparable to the oxygen concentration – the methane concentration in the post-suspension phase reaches the level of the pre-incubation phase.

Slurry experiment

To determine the kinetics of microbial methane oxidation of a sediment suspension, an additional slurry experiment was carried out. For this, the sediment from an additional core was stirred up with the propeller and subsamples ($n = 13$) of the sediment–water suspension were taken at the water outlet. These aliquots (11 ml, approximately 1 ml sediment and 10 ml water) were transferred to glass tubes (27 ml) closed with butyl stoppers. Methane was added via a syringe to the headspace to get different concentrations. The tubes were then continuously rolled lengthwise to keep the sediment in suspension. The tubes were incubated at 7 °C in the dark. Subsamples of the gas phase were analyzed for their methane concentration. Control tubes were run with autoclaved sediment to check for abiotic methane decrease.

The potential methane oxidation (f_{slurry}) was described best by the following formula: $c_t = c_0 \cdot \exp(-k \cdot t)$, with c_t = methane concentration at a certain time, c_0 = initial concentration, k = velocity constant and t = elapsed time.

The maximal methane oxidation rate $v_{\max}$ [μmol l^{-1} h^{-1}] and the half saturation constant K_s [μmol l^{-1}] were calculated using an Eadie–Hofstee transformation (Lehninger 1985).

Results

The continuous water flow microcosms

To test whether the methane concentration in the sediment changed due to maintaining the cores in the experimental set-up, two control cores were compared with two sediment cores freshly retrieved from the study site. There was no significant difference in the methane concentrations of the top 0.5 cm ($n = 9$, $p = 0.49$, unpaired t-test after rank transformation of the data) or in the other depths. In the water column of the control cores, methane concentrations were 0.34 ± 0.13 μmol l^{-1} in winter and 0.28 ± 0.06 μmol l^{-1} in summer, which was the same range as found *in situ*.

Methane leakage through the lids of the cores and fittings in the experimental set-up was checked with a microcosm only filled with water and was recorded as 1% per hour over 20 h.

In the control cores the average oxygen concentration of the water column was 349 ± 4 μmol l^{-1} in winter (7 °C) and 291 ± 9 μmol l^{-1} in summer (14 °C). The minimum oxygen concentration during a resuspension event never dropped below 256 μmol l^{-1} in winter and 222 μmol l^{-1} in summer.

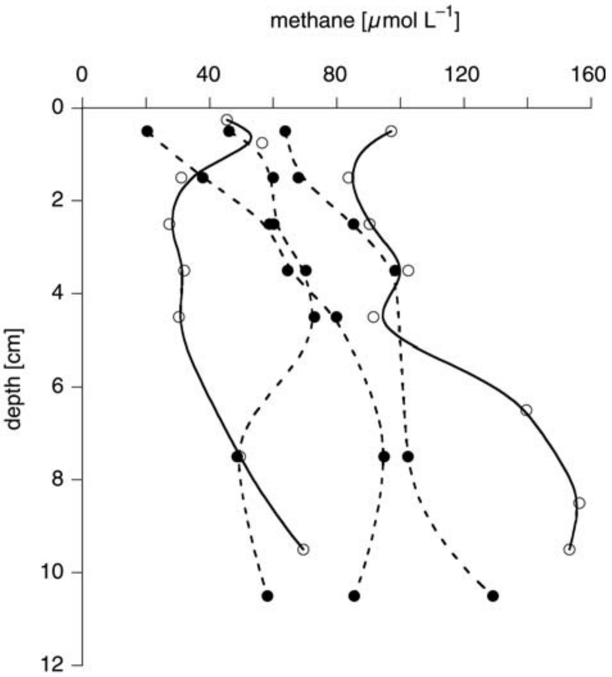

Figure 1. Methane in the sediment, in winter (open circles, $n = 2$) and in summer (filled circles, $n = 3$).

In situ *concentrations of methane*

In winter, methane concentrations in the two sediment cores ranged from 31 to 97 μmol l^{-1} in the top 2 cm of the sediment (Figure 1). At 2–6 cm depth, methane concentrations decreased towards 20 and 80 μmol l^{-1}. Below this, the methane concentration increased again to maximal values of 60 and 140 μmol l^{-1} at 10 cm depth. In summer, the methane concentration at the surface of the three sediment cores ranged from 20 to 67 μmol l^{-1}, and increased continuously with depth to reach a maximum of 100 μmol l^{-1} at 10 cm sediment depth (Figure 1). Methane concentrations in the water column were 0.31 ± 0.21 μmol l^{-1} ($n = 11$) in winter and 0.30 ± 0.24 μmol l^{-1} ($n = 13$) in summer.

With the *in situ* methane sensor three major resuspension events were observed on 12 April 2004. The first suspension event started at 4:44 and lasted 5 h, the second one started at 12:56 lasting for 50 min and the third one started at 17:04 lasting for 1 h: 50 min (Figure 2). Concentrations during resuspension ranged from 1.66 to 2.14 μmol l^{-1}, in between the resuspension events concentrations dropped to 0.27–0.30 μmol l^{-1} and dropped further to 0.01 μmol l^{-1} at the following day.

Resuspension of sediment in the microcosms

Resuspension of sediment in the core tubes resulted in a pulsed release of methane into the water column. In the winter cores, methane concentrations in the overlying water increased from an initial value of 0.29 ± 0.17 μmol l^{-1} in the three cores to 0.73 ± 0.06 μmol l^{-1} (core W_a), 1.62 ± 0.18 μmol l^{-1} (core W_c) and 5.80 ± 0.77 μmol l^{-1} (core W_b) during the resuspension phase. In the summer cores, methane concentrations in all three replicates increased to a very similar extent, from 0.47 ± 0.14 μmol l^{-1} to 1.11 ± 0.24 μmol l^{-1} with only small differences between the three parallel cores.

The measured methane flux in the control cores was always low, with 12 ± 11 μmol h^{-1} m^{-2} in winter and 6 ± 4 μmol h^{-1} m^{-2} in summer, while diffusive fluxes calculated from the pore water profiles were maximal 2.3 μmol h^{-1} m^{-2}. The diffusive flux was calculated for the top 5 cm of the summer cores (Figure 1).

In winter, resuspension of the sediment resulted in an almost pulse-like increase of the flux to 44 ± 5 μmol h^{-1} m^{-2} for core W_a, 114 ± 14 μmol h^{-1} m^{-2} for core W_c and 430 ± 59 μmol h^{-1} m^{-2} for core W_b (Figure 3a). Averaged over all three cores, a mean methane flux of 207 ± 176 μmol h^{-1} m^{-2} was calculated for a resuspension event in winter. Methane flux in the summer cores was lower and more homogenous compared to the winter, with average values of 64 ± 12 μmol h^{-1} m^{-2} for core S_c, 71 ± 23 μmol h^{-1} m^{-2} for core S_a and 89 ± 3 μmol h^{-1} m^{-2} for core S_b (Figure 3b). Averaged over all three cores, a mean methane flux of 73 ± 18 μmol h^{-1} m^{-2} was calculated for a resuspension event in summer.

During the resuspension phase in winter, a maximum of 3749 mg l^{-1} suspended solids were dispersed in core W_c while only 1318 and 843 mg l^{-1} suspended solids were measured in the other two cores (W_a and W_b). During

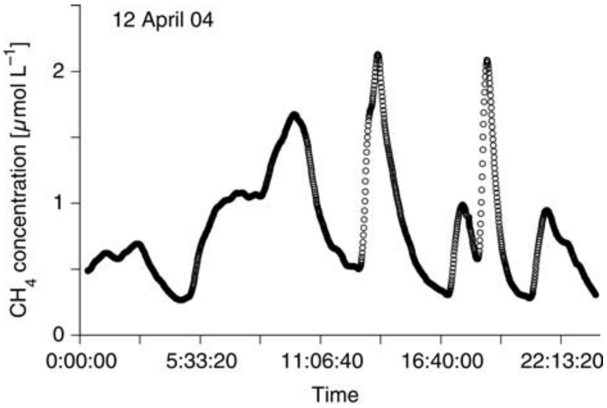

Figure 2. Methane concentrations in the water column recorded with a methane sensor, at 12.04.2004. Sensor data were calibrated against headspace analysis and smoothed over 10 min.

summer, sediment resuspension led to maximum values of 3930 mg l^{-1} suspended solids in core S_c but only 1606 and 429 mg l^{-1} were suspended in the cores S_a and S_b. No correlation was found between the amount of suspended solids and the methane flux (Spearman rank correlation, $\rho = -0.14$, $n = 6$) during winter or summer in either set of cores.

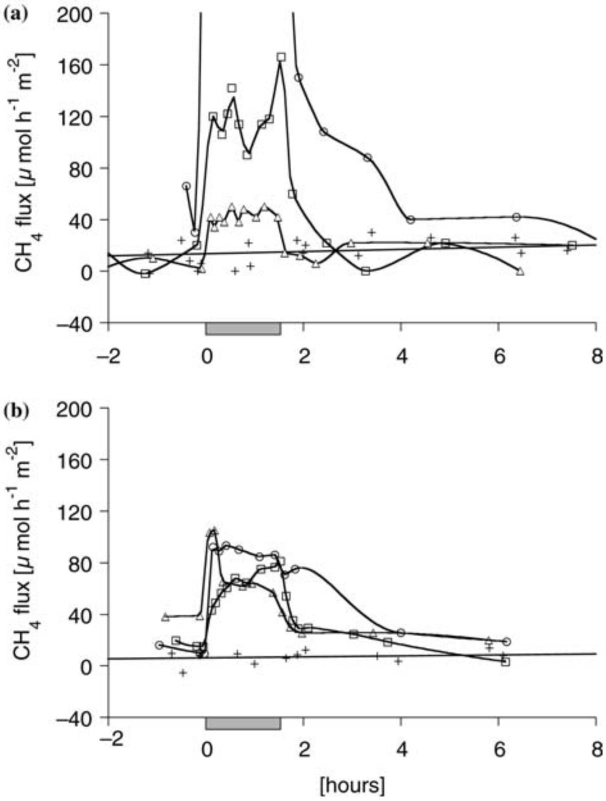

Figure 3. Methane flux from the sediment cores during a resuspension event (shaded area). The suspension event lasted 1.5 h (t = 0–1.5). Three parallel cores are shown in winter (A) with the cores W_a – △, W_b – ○ and W_c – □ and in summer (B) with the cores S_a – △, S_b – ○ and S_c – □. The regression lines are drawn for three undisturbed control cores (+), in winter and summer.

Estimation of methane oxidation rates

After the propeller stopped in the treatment cores (1.5 h after the start of the resuspension event), the methane concentration in the overlying water of core W_a was still low (0.72 μmol l^{-1}, Figure 4, upper graph) and decreased rapidly to the average methane level of the control cores in less than 1 h. Therefore, no reliable methane oxidation rate could be calculated for this core. In core W_b, the methane concentration was highest at the end of the resuspension phase with 6.74 μmol l^{-1} and was still slightly above the control values after 3–4 h. A MOX_{exp}-rate of 2.42 μmol l^{-1} was calculated for the standardized integration

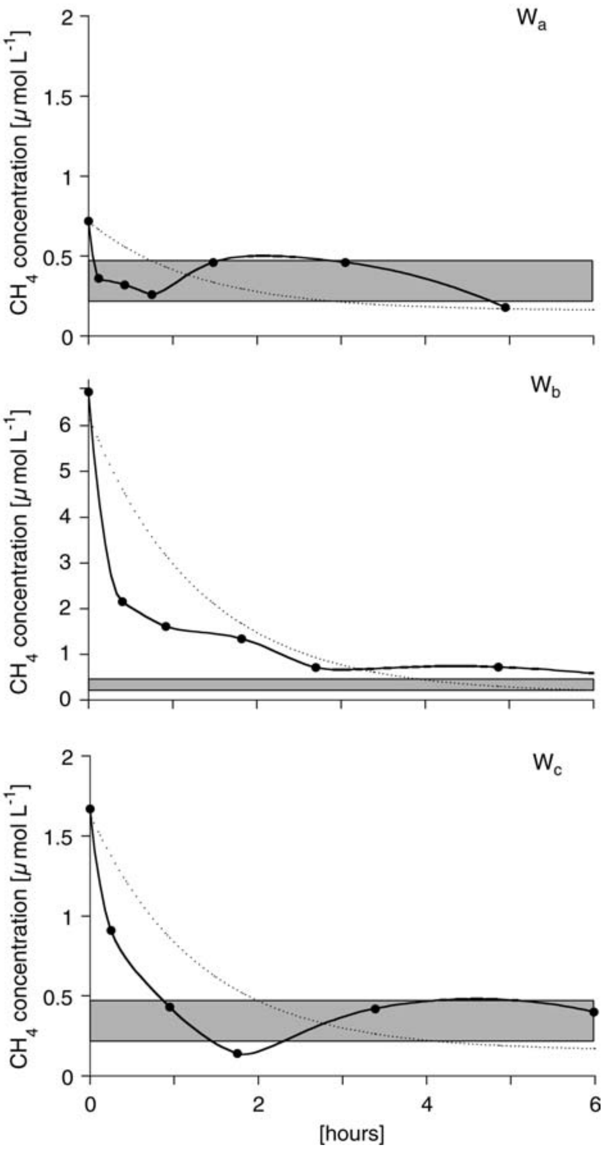

Figure 4. Decrease of methane concentrations in the overlying water after sediment resuspension ($t = 0$), for the three winter cores (W_a, W_b, W_c). The filled circles show the measured values and the dotted line shows the dilution and loss of methane. The shaded area is the concentration range of the control cores. Note the different scale for core W_b.

time of 3 h for this core. This represents 16% of the real methane loss in this core (Table 1). In core W_c (Figure 4, lower graph), the methane concentration after the resuspension phase was 1.67 μmol l^{-1} and reached the values of the control cores after about 1 h. A standardized MOX_{exp}-rate of 0.86 μmol l^{-1} per 3 h was calculated for this core representing 23% of the real methane loss. From the independent slurry experiment, the percentage of the potential methane oxidation rate (MOX_{pot}) from the real loss was 10% for core W_b and W_c.

In the summer cores, the methane concentration at the end of the resuspension event (after the propeller stopped) was almost the same for all three cores (0.91–1.27 μmol l^{-1}) (Figure 5). In core S_c, the methane concentration reached the control values after 3 h and therefore more slowly than in the winter cores. The standardized MOX_{exp}-rate over 3 h in this core was calculated to be 0.20 μmol l^{-1} or 10% of the real loss (Table 1). From the independent slurry experiment, the percentage of potential methane oxidation rate (MOX_{pot}) from the real loss was 12% for core S_c.

In the cores W_b, S_a and S_b, the methane concentrations in the overlying water were still well above the control values, even after 5 h (Figures 4 and 5). Therefore, no integral calculation of the methane oxidation rate was possible for these three cores.

Slurry experiment

To determine the kinetics of methane oxidation in resuspended sediment, an independent slurry experiment was performed. Methane concentration decreased exponentially with time (data not shown). The velocity constant, k was 0.051 $\pm$ 0.01, $n = 10$ and using this the potential methane oxidation rate was calculated.

The microbial methane oxidation rate was dependent on the methane concentration (Figure 6). Applying a linearization according to Eadie–Hofstee, the maximal methane oxidation rate v_{max} was calculated to be 10 μmol h^{-1} l suspension^{-1} with a half saturation constant K_s of 7 μmol l^{-1}. If the parameters were related to sediment volume, a maximal rate of 115 μmol h^{-1} l sed^{-1} was obtained.

Discussion

Continuous water flow microcosms

A continuous water flow microcosms was chosen as the experimental set-up but this implies also that the measured parameters are permanently diluted. Sediment resuspension strongly increases oxygen consumption through the oxidation of suspended reduced compounds (Christiansen et al. 1997; Laima et al. 1998) and, because aerobic methane oxidation stops when the oxygen

Table 1. Methane oxidation rate in the water after the end of the resuspension event.

Core	Season	MOX_{exp} [μmol l^{-1}] = $\int_0^3$ dil + loss − $\int_0^3$ meas	MOX_{pot} [μmol l^{-1}] = $\int_{0h}^{3h}$ hypo − $\int_{0h}^{3h}$ slurry	MOX_{exp} in % of the real loss	MOX_{pot} in % of the real loss
W_b	Winter	2.42	1.46	16	10
W_c	Winter	0.86	0.36	23	10
S_b	Summer	0.20	0.26	10	12
Average				16 ± 7	11 ± 1

concentration drops below ca. 10% air saturation (Frenzel et al. 1990), the oxygen concentration of the overlying water is critical. The continuous water flow microcosms buffers this effect and oxygen saturation was always greater than 66%. This set-up is therefore more close to the *in situ* situation, where suspended sediment is diluted into a big and well-aerated volume of overlying water.

The sediment was eroded by the motion of a model ship's propeller, as described in other resuspension studies (Christiansen et al. 1997; Laima et al. 1998). During the resuspension in this study the sediment load of the overlying water column was 1676–1975 mg l^{-1} of suspended solids. This is somewhat higher than the 425 and 890 mg l^{-1} of similar experiments (Spagnoli and Bergamini 1997; Garstecki et al. 2002). About 5 mm of sediment was eroded, comparable to observations of bioturbation by fish. At the study site, bream (*Abramis brama* L.) have been observed to take bites out of the sediment. The resulting 'hollows' are about 7 cm in diameter and 1 cm deep (Ph. Fischer, unpublished data).

When the amount of methane in the top 5 mm (as measured in the pore water profiles) would be diluted into the overlying water of the experimental cores, methane concentrations would increase to similar values (2.7 ± 1.4 μmol l^{-1} compared to 1.1 and 2.9 μmol l^{-1} measured in the experiments).

The diffusive methane flux calculated from pore water profiles was much lower but within the range of the measured fluxes. The chosen experimental set-up was not sensitive enough to determine the methane flux in the control cores precisely. This is reflected in the high standard deviations. Other reasons for the higher measured fluxes in the control cores may be background bioturbation or bubble formation. Visible bubble formation was never observed, however it can not be excluded (Bazhin 2003). However, comparing the flux rates of the control cores with the cores with sediment resuspension it is obvious that the control values are much lower than in the cores with suspended sediment.

With the *in situ* methane sensor it is possible to measure methane concentrations of the water column during calm and during stormy conditions. The correlations between the increase of methane concentrations and turbidity (as indicator for resuspension) or wind will be investigated in another study. For

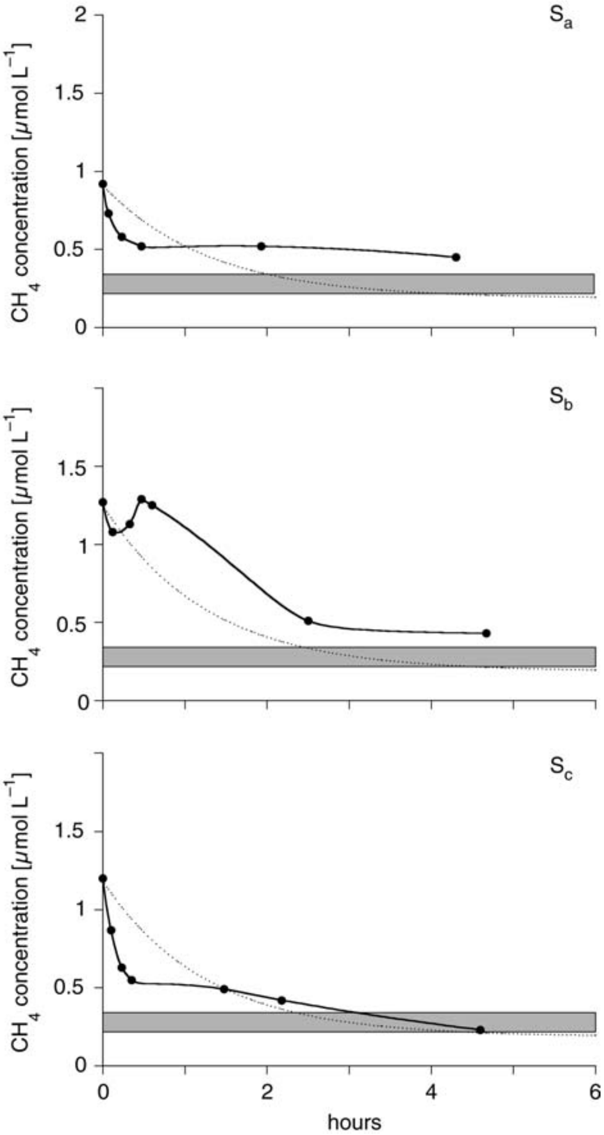

Figure 5. Decrease of methane concentrations in the overlying water after sediment resuspension ($t = 0$), for the three summer cores (S_a, S_b, S_c). The filled circles show the measured values and the dotted line shows the dilution and loss of methane. The shaded area is the concentration range of the control cores.

this study however, it can be stated that with the experimental set-up the methane concentrations and the duration of increased methane concentrations simulated quite well the observed *in situ* values.

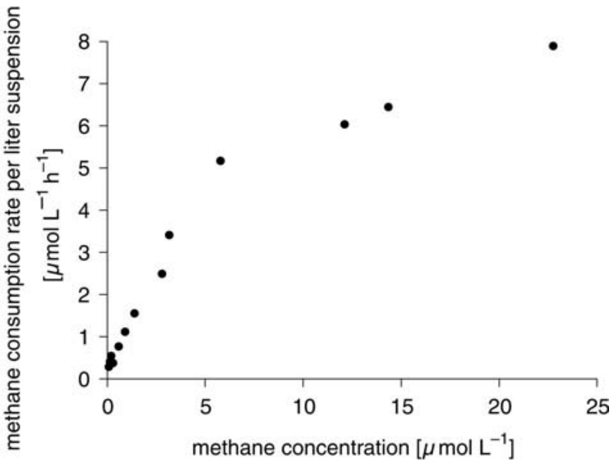

Figure 6. Dependence of the methane consumption rate (μmol h^{-1} per liter sediment suspension) on the methane concentration.

Seasonality and variability of the cores

In this study two series of experiments were performed, one to assess the winter situation and one for the summer situation. For the *in situ* methane concentrations in the sediment, there was a high variability between the cores, but no distinct difference between winter and summer. Also the methane fluxes from winter and summer experiments were comparable, with the exception of core W_b.

Higher methane concentrations in the sediment and, therefore, higher fluxes after sediment resuspension, were expected in summer (Thebrath et al. 1993). However, several of our measurements of methane profiles in the sediment at the study site show no clear seasonal pattern. This discrepancy may be explained by a high interannual variability of methane concentrations in sediments (Nakamura et al. 1999) or bubble formation (Bazhin 2003). Additionally, for methane flux the 'history' of each core is important, e.g. how often has the sediment been disturbed before and what was the methane concentration in the erodable sediment depth. Different concentrations in the erodable sediment depth will then determine the amount released by sediment resuspension. At this exposed study site the frequency of sediment resuspension may be more important for the methane concentrations in the sediment than the seasonality of methane production.

Methane concentrations

Methane concentrations in the overlying water of the control cores, and in the water column at the study site, were very similar (around 0.3 μmol l^{-1}) and also similar to another study on the *in situ* methane concentrations in a sheltered bay at a nearby sampling site (0.4 μmol l^{-1}, Schmidt and Conrad 1993). However, lower concentrations (0.08–0.2 μmol l^{-1}) have been reported for the northern shore of Lake Constance (Schulz et al. 2001).

The resuspension of sediment, as simulated in the microcosms, resulted in an increase of the methane concentration in the water column to 1.11 ± 0.24 μmol l^{-1} in summer (max 1.55 μmol l^{-1}) and 2.86 ± 2.32 μmol l^{-1} in winter (max. 6.74 μmol l^{-1}). Compared to the background concentration of methane, this is a 5-fold increase for the summer and a 20-fold increase for the winter situation. Similar results are reported for a Japanese lake, where the suspension and advection of bottom sediment was a major source of methane in the water column, leading to a 3-fold increase in methane concentrations (Sakai et al. 2002).

Fluxes of methane across the air–sea interface were computed according to Wanninkhof (1992) at 7 and 14 °C. Expected equilibrium concentrations of methane in lake water were calculated according to the equation of Wiesenburg and Guinasso (1979), by applying an average atmospheric mixing ratio of 1.875 ppmv (http://www.cmdl.noaa.gov/ccgg/iadv/ station 'Ochsenkopf', Germany). For a calm situation (control) a wind velocity of 0.5 m s^{-1} and for a resuspension event a wind velocity of 5 m s^{-1} were assumed (wind data from 1.1.2001 to 31.8.2001, Wetterstation Konstanz). Under calm conditions the methane flux into the atmosphere would range from 4 to 5 μmol m^{-2} d^{-1}. If strong winds lead to sediment resuspension the methane flux into the atmosphere would increase by three orders of magnitude to 1.7 mmol m^{-2} d^{-1} in summer and 3.7 mmol m^{-2} d^{-1} in winter. Flux calculations of other authors with *in situ* methane concentrations at a nearby study site (323–882 μmol m^{-2} d^{-1}) lay in between of the experimental data of this study (Schmidt and Conrad 1993).

Sediment resuspension in the littoral zone

The sediment resuspension in the microcosm resulted in a large flux of methane into the water column (207 ± 176 μmol h^{-1} m^{-2} in winter and 73 ± 18 μmol h^{-1} m^{-2} in summer). However, extrapolation of the experimental data to standard time (h) and standard area (m^{-2}) is critical because there are different reasons for sediment resuspension in the littoral.

Bioturbation by benthivorous fish is one reason for sediment resuspension. Bream especially are known to be responsible for an increase of suspended sediment and nutrient concentrations in the water of a whole lake (Tolonen et al. 2000). Unfortunately, no exact data are available on the biomass and activity of these fish in the littoral of Lake Constance. Thus, one can only estimate that the feeding activity of bream results in a short time of sediment resuspension, but as they bite and dig deep into the sediment this will result in significant but locally restricted methane flux.

The currents in Lake Constance are mainly dominated by the basin-wide, wind-driven circulation, which, in the littoral, is mostly directed along the shore (IGKB 1987; Bäuerle et al. 1998). Strong winds or storms enhance the lake circulation, causing strong and deep currents able to resuspend sediment. The amount of sediment resuspended by such currents is certainly lower than that due to bioturbation, but the currents and the concurrent sediment resuspension may, however, last for a few hours and therefore a much longer time. Strong winds (> 5 m s^{-1}) last on average 2.7 h, but most frequently for 1 h (wind data from 1.1.2001 to 31.8.2001, Wetterstation Konstanz). Wave action, either driven by wind or ship movements, is another reason for sediment resuspension. In the littoral zone, wind-induced waves are the most frequent reason for sediment resuspension. They are much more efficient than ship waves as they act for much longer and are normally accompanied by alongshore currents.

Unfortunately there are no reliable data on the frequency and intensity of sediment resuspension available for Lake Constance. The simulated sediment resuspension of 1.5 h and an average load of 1423 mg l^{-1} in this study can be regarded as intermediate between the two natural extremes of intense but short sediment resuspension through bioturbation and long-lasting but weaker sediment resuspension by water currents. First results from the *in situ* methane sensor also support this assumption.

The importance of sediment resuspension for the methane flux is demonstrated by the following estimations. The area of the littoral zone (6.51 km^2) of the Überlingersee (58.73 km^2) is quite small with 6.5% (Ostendorp et al. 2003). The methane flux from undisturbed sediment into the water of whole littoral of the Überlingersee amounts to 1875 mol d^{-1} (based on the methane flux data of the control cores). The question is how many km^2 of littoral sediment have to be resuspended to be important for the total flux? To reach the same flux by resuspension as by the whole undisturbed zone about 1.1 km^2 of littoral sediment have to be resuspended for the summer situation and 0.4 km^2 in winter (based on the methane flux data during resuspension of the summer and winter cores). Thus only 6–16% of the littoral zone has to be resuspended to reach the same flux as from undisturbed littoral sediment. The temporal aspect of resuspension is demonstrated by the question how long has the sediment be in resuspension to be important for the daily flux of the undisturbed sediment. In summer, a sediment resuspension lasting for 3.9 h is sufficient to reach the undisturbed daily flux (288 μmol m^{-2}). In winter only 1.4 h of resuspension are necessary to reach this amount.

Methane oxidation

In undisturbed sediment about 79% of the methane diffusing upwards is oxidized at the sediment surface (Bosse et al. 1993). In contrast, only 16 ± 7% of the released methane was oxidized in this study on sediment resuspension. The methane oxidation by methanotrophic bacteria was estimated for three simulated sediment resuspension events (W_b, W_c and S_c). Because some assumptions had to be made for the calculation of the methane oxidation rate, the results were crosschecked with an independent method using a slurry experiment. With this method, an average of 11% of the real loss of methane was oxidized. Thus, the assumptions made in the main calculation are thought to be correct. The significantly lower efficiency reported in this study may have several reasons.

The maximal methane oxidation rate, v_{max}, is the rate measured at optimal methane and oxygen supply in diluted suspensions. It is a relative measure for the population size and activity of methane oxidizing bacteria and enables a comparison between different studies. Kinetic parameters are either related to sediment or water volume. The kinetic parameters from the slurry experiment of this study (v_{max} = 115 μmol h^{-1} l sed^{-1}) show the same characteristics as other freshwater sediments (13–35 μmol h^{-1} l sed^{-1}, Buchholz et al. 1995; 83 μmol h^{-1} l sed^{-1}, Roy et al. 1996). In the water column these parameters are much lower, v_{max} = 2–6 μmol h^{-1} l $water^{-1}$ and half saturation constants K_s = 6–44 μmol l^{-1} (Liikanen et al. 2002). For the sediment resuspension in this study v_{max} and Ks are related to the volume of the sediment suspension (v_{max} = 10 μmol h^{-1} l $suspension^{-1}$; K_s = 7 μmol l^{-1}) and are comparable to values for the water column. This indicates that the methane oxidation rate is limited by the low methane concentration, even during resuspension (1.6–2.9 μmol l^{-1}, average of the resuspension phase of all three cores in summer and winter, respectively). Several studies have found that in freshwater systems, methane oxidation rates are mainly controlled by the availability of substrates, methane and oxygen (Striegl and Michmerhuizen 1998; Liikanen et al. 2002)

The low efficiency of the methane oxidizing bacteria may also be due to inhibitory compounds released from deeper sediment layers. High concentrations of some inorganic compounds have a negative effect on the growth of methanotrophs (Bussmann et al. 2004), but at least the concentration of phosphate (45 μmol l^{-1}) and nitrate (14 μmol l^{-1}) during the sediment resuspension are well below these concentrations. Interactions between methanotrophs and inorganic and organic particles are ambiguous; clay particles have a positive effect on methane oxidation, while living algae and $CaCO_3$, $CaPO_4$ inhibit methane oxidation (Weaver and Dugan 1972). Thus the overall effect of suspended sediment, containing all these substances remains unknown.

Methane production

In undisturbed sediment the diffusive methane flux into the water column is based on the methane production in deeper sediment layers minus the methane oxidation at the sediment surface. During sediment resuspension, the methane flux is based on the instantaneous release of the methane dissolved in the suspended sediment plus the still on-going flux from the deeper sediment layers. After resuspension has finished, the latter flux is still going on. Methanotrophic bacteria from the sediment surface are also diluted into the water column, and are hardly able to buffer the methane release, as shown in this study.

The question is what happens at the new sediment surface, after resuspension has stopped? In some cases (cores W_b, S_a and S_b), the methane flux increases above the control values, therewith indicating an increased methane production. Methane production, which occurs in 2–5 cm depth (Thebrath et al. 1993), should not be affected directly by the resuspension of 0.5 cm sediment. However, the sudden availability of oxygen in the until-now anoxic sediment layers may enhance decomposition of organic material and therefore also lead to an enhanced methane production. In some cases (cores W_a, W_c and S_c) the methane flux level back into the range of the control cores, therewith indicating that the new surface was quickly 'sealed' again by methane oxidation. Methanotrophic bacteria at the new sediment surface should quickly (1–7 h) return into an active state (Roslev and King 1996). At the new surface the diversity and community structure of methanotrophic bacteria is probably the same as before (Pester et al. 2004). Also the oxygen concentration in the top 3 mm reached the original condition within 0.5 h (Gerhardt et al. unpublished data). From this study it cannot be deduced which factor of the methane flux, methane production or methane oxidation is more influenced by sediment resuspension, as there are three examples for each situation.

This study shows that sediment suspension events in the littoral zone lead to variations in methane flux over several orders of magnitude. Hence, sediment resuspension events have to be taken into account for any calculations of the cumulative methane flux from the littoral zones. However, for such irregular events, *in situ* measurements of methane concentration and turbidity are essential in order to assess more precisely the duration and intensity of such events. The time scale of such resuspension events does not match up with the capabilities of methane oxidizing bacteria, since they could buffer the methane release only to 16%. Therefore the export of methane from the littoral sediment into the water column, or into the atmosphere, can occur almost unaffected by the activity of methane oxidizing bacteria.

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